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(56) Documents Cited

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(54) Superconducting materials

(57) A starting powder of the formula

$SE_uM_vCu_wO_x$, where

SE = Y, Nd, Sm, La, Dy, Er or Gd, or a mixture of two or more of these elements

M = Ba, Sr or Ca, or a mixture of two or more of these elements

u = 0.8 to 2

v = 1 to 2

w = 3 to 4 and

x = $1.5u + v + (0.5 \dots 1.5)w$,

is mixed with a specific platinum-containing compound of the formula

$SE_kPt_lM_mCu_nO_x$, where

k = 0 to 2

l = 1 to 2

m = 2 to 4

n = 1 to 2

and

x = $1.5k + m + (n + 1)z$, where ($z = 0.5 \dots 2$),

in a mole fraction of 0.2 to 7 mol % and solid materials in the form of, for example, blocks, moulded bodies, strips are produced from this mixture by comminution and compression, as well as heat treatment, which may include a melt-texturing process without a crucible. These solid materials may be used as superconductors in power, drive and transport engineering.

The specific platinum-containing compound is claimed.

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A PROCESS FOR PRODUCING A HIGH-TEMPERATURE SUPERCONDUCTING SOLID MATERIAL

The invention relates to a process for producing a high-temperature superconducting, melt-textured solid material which, in the form of blocks, moulded bodies, strips and the like, may be used, for example, in power, drive and transport engineering.

It is already known to produce solid high-temperature superconducting materials through peritectic crystallisation

α -superconductor phase (solid material) \leftrightarrow melt + β -solid phase,

which takes place as an α -phase in air at 1020°C for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO). Non-reacted β -solid phase $\text{Y}_2\text{BaCu}_3\text{O}_x$ (211) remains as an inclusion in the structure in the case of YBCO. The crystallisation on which this process is based, together with a temperature gradient, is called melt texturing.

In this case it is common practice to firstly compress pulverulent starting material into moulded bodies. These are heated in a melting step to beyond the peritectic melting temperature. The melt is then homogenised by means of a holding step far above this temperature. The temperature is afterwards lowered rapidly to just above the peritectic melting temperature to cause crystallisation, which takes

place with low cooling rates in temperature ranges below that at which peritectic decomposition occurs and results in the textured structure.

If the starting powder only consists of high-temperature superconducting material, a high proportion of melt escapes from the moulded body with disadvantageous effects when the peritectic temperature is exceeded. This entails a deterioration in or even a loss of superconducting properties. Moreover, the melt which has escaped may react with the crucible material, resulting in a further deterioration in the superconductor properties.

It is already known to use starting powder containing additives to prevent melt from escaping in this way. For example, $\text{Y}_2\text{BaCu}_3\text{O}_7$ and Y_2O_3 are added for YBCO to lower the reaction temperature and reduce the 211 inclusions to a certain degree (G. Krabbes et al Physica C 244 (1995) 145-152). However the disadvantage in this case lies in the occurrence of an inhomogeneous grain size distribution of the inclusions and cracking.

A certain improvement is achieved by carrying out the homogenisation step in a platinum crucible and at a temperature of 1200°C , afterwards quenching the melt to ambient temperature and then processing it into powder. The starting powder which is thus formed is extremely sensitive to air and moisture and, because of the additional expenditure which this method entails, its production requires high process costs. A further disadvantage lies in the fact that the 211 inclusions are still distributed inhomogeneously in the superconducting solid materials produced from this powder. These disadvantages cannot be eliminated even by adding Pt or PtO_2 and limiting the temperature to 1100°C . Although other non-specific additives such as BaTiO_3 , BaCeO_3 and BaSnO_3 (Ch.- J. Kim et al J. Mater. Sci. Lett. 11 (1992) 831; Ch.- J. Kim, P.J. McGinn,

Physica C 222 (1994) 177; W. Gawalek et al Cryogenics 33 (1993) 65) enable the process costs to be reduced, these cannot prevent the 211 inclusions from being inhomogeneously distributed or prevent cracking. One reason for this lies in the fact that these additives react with the peritectic melt and lead to the formation of secondary phases which disturb the equilibrium. This results in the melt texturing process being severely disturbed and becoming difficult to control and reproduce.

The object of the invention is to create a method for producing high-temperature superconducting, melt-textured solid materials such that it entails low process costs and such that 211 precipitations which develop in the material are distributed as homogeneously as possible and have a small grain size, and that cracking is largely prevented.

The invention lies in the fact that a starting powder of the formula



where

- SE = Y, Nd, Sm, La, Dy, Er or Gd or a mixture of two or more of the above elements
 M = Ba, Sr or Ca or a mixture of two or more of the above elements
 u = 0.8 to 2

$$v = 1 \text{ to } 2$$

$$w = 3 \text{ to } 4 \text{ and}$$

$$x = 1.5 u + v + (0.5 \dots 1.5) w,$$

is mixed with a specific platinum-containing compound of the formula



$$k = 0 \text{ to } 2$$

$$l = 1 \text{ to } 2$$

$$m = 2 \text{ to } 4$$

$$n = 1 \text{ to } 2$$

and

$$x = 1.5 k + m + (n + 1)z, \text{ where } (z = 0.5 \dots 2),$$

in a mole fraction of 0.2 to 7 mol %, and that a high-temperature superconducting material is produced from this mixture by comminution and compression, in addition to heat treatment, which, preferably, includes a melt-texturing process without a crucible.

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According to a preferred embodiment of the invention, $YBa_2Cu_3O_{7-\delta}$ or $Nd_{1+y}Ba_{2-y}Cu_3O_{7-\delta}$, where $y = 0 \text{ to } 0.06$ and $\delta = 0 \text{ to } 1$, may be used as the starting material and $PtBa_4Cu_7O_{13}$ added as the specific platinum-containing compound in a mole fraction of 2 mol %.

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The specific platinum-containing compound is preferably produced by means of a powder technology synthesis process.

The proposed method advantageously results in dimensionally stable high-temperature superconductor materials with high frozen-in residual fields and critical current densities, as required in power and transport engineering.

The addition according to the invention of a platinum-containing compound to the starting powder before partial melting does not change the peritectic crystallisation on which the melt texturing process is based. The usual process temperatures and parameters, such as heating rates, holding times and cooling rates, can be maintained, although the method is advantageously less sensitive to fluctuations in the process parameters.

The specific additive according to the invention increases viscosity and lowers interfacial tension in a manner similar to that of a non-specific additive, although has the additional advantage of helping to establish and maintain the equilibrium of the melt. There are no reactions giving

rise to unwanted secondary phases which impair the properties. As a result, the melt texturing process and the development of the superconductor phase proceed in a more stable and reproducible manner. One advantage lies in the fact that the amount of melt which escapes and thus the possibility of a reaction occurring with the crucible material remain slight. This means that there is no appreciable contamination or degradation, which is linked with this, of the superconducting properties in the melt-textured material.

The 211 precipitations which develop are characterised by a very small grain size and by a homogeneous distribution over the entire sample volume. The development of cracks is greatly reduced or prevented entirely by the near-equilibrium crystallisation.

The invention is illustrated in detail in the following on the basis of embodiments.

Example 1

2 mol % of a pulverulent specific compound of the composition $\text{PtBa}_2\text{Cu}_2\text{O}_7$, and 24 mol % of pulverulent Y_2O_3 , are mixed with a commercially available starting powder of the high-temperature superconducting compound $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. The above-mentioned specific compound was produced beforehand from Y_2O_3 , BaCO_3 , CuO and Pt by means of an adapted powder technology synthesis process.

The powder mixture obtained is firstly comminuted and then compressed uniaxially to form cylindrical moulded bodies of a length of 15 mm and a diameter of 30 mm or cuboid moulded bodies of the dimensions $27 \times 27 \times 10 \text{ mm}^3$. The moulded bodies are then heated at 300 K/h to 1150°C and maintained at this temperature for 20 minutes, after which the temperature is

lowered to 1120°C. Finally, melt texturing is carried out by cooling at 6 K/h with a temperature gradient of 20 K/cm.

The structure of the high-temperature superconducting moulded bodies which are thus produced consists of crystals which are several cubic centimetres large and have different orientations. The 211 precipitations are distributed very finely and homogeneously. The melt loss is insignificant, in spite of the temperatures employed, which are distinctly higher than the temperature at which the peritectic melt forms ($\sim 1020^\circ\text{C}$).

Following the final, necessary step of charging with oxygen at 370°C, the critical current density of the moulded bodies is greater than 10^4 A/cm² at 77 K and 0 T.

Example 2

Cylindrical moulded bodies of a length of 15 mm and a diameter of 30 mm are produced by compression from the powder mixture described in Example 1, consisting of starting powder, specific compound and Y_2O_3 , with a Sm-123-nucleus being added to each of the moulded bodies before compression. The moulded bodies, which are compressed as in Example 1, are heated at 300 K/h to 1050°C and textured at a cooling rate of 0.5°C/h. The melt loss is slight in this case as well, in spite of the low rates of cooling and the long process times which these entail.

The structure of the moulded bodies thus produced consists of one to two crystals which exhibit the preferred orientation of the Sm-123-nucleus.

Following a final step of charging with oxygen at 370°C over 72 h in a flowing oxygen atmosphere, the high-temperature superconducting moulded bodies thus produced have a frozen-in residual field of 550 mT and a levitation force of 50 N

at 77 K. The critical current density of the moulded bodies is greater than 10^4 A/cm² at 77 K and 0 T.

Example 3

2 mol % of a pulverulent specific compound of the composition $\text{PtBa}_2\text{Cu}_3\text{O}_7$, and 40 mol % of pulverulent Nd_2BaO_4 , are mixed with a starting powder of the composition $\text{NdBa}_2\text{Cu}_3\text{O}_{7-x}$. The above-mentioned specific compound was produced beforehand from Y_2O_3 , BaCO_3 , CuO and Pt by means of an adapted powder technology synthesis process.

After comminution, the powder mixture is compressed uniaxially to form cylindrical moulded bodies of a length of 6 mm and a diameter of 14 mm. The moulded bodies are then melt-textured in a nitrogen/oxygen atmosphere with only 1 % by volume O_2 . For this purpose the moulded bodies are heated to 1100°C and, starting from 1040°C, cooled to ambient temperature by cooling at 1 K/h with a temperature gradient of 2 K/cm. No appreciable melt loss occurs during the melt texturing.

The high-temperature superconducting moulded bodies thus produced have a structure which is characterised by a plurality of crystals and very small, homogeneously distributed Nd-422 inclusions of a size of $< 5 \mu\text{m}$.

Following the final oxygen charging step, the critical current densities of the moulded bodies are $> 10^4$ A/cm² at 77 K and 0 T.

CLAIMS

1. A process for producing a high-temperature superconducting, melt-textured solid material, using a superconducting starting material comprising an additive, characterised in that a starting material of the formula



where

SE = Y, Nd, Sm, La, Dy, Er or Gd, or a mixture of two or more of these elements

M = Ba, Sr or Ca, or a mixture of two or more of these elements

u = 0.8 to 2

v = 1 to 2

w = 3 to 4

and

x = $1.5 u + v + (0.5 \dots 1.5)w$,

is mixed with a specific platinum-containing compound of the formula



where

k = 0 to 2

l = 1 to 2

m = 2 to 4

n = 1 to 2

and

x = $1.5 k + m + (n + 1)z$, where ($z = 0.5 \dots 2$),

in a mole fraction of 0.2 to 7 mol %, and a high-temperature superconducting solid material is produced from this mixture by comminution and compression, in addition to heat treatment.

2. A process as claimed in claim 1, wherein said heat treatment includes a melt-texturing step without a crucible.

3. A process as claimed in claims 1 or 2, wherein $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ or $\text{Nd}_{1+y}\text{Ba}_{2-y}\text{Cu}_3\text{O}_{7-\delta}$, where $y = 0$ to 0.06 and $\delta = 0$ to 1 , is used as the starting material and $\text{PtBa}_4\text{Cu}_2\text{O}_9$ is added as the specific platinum-containing compound in a mole fraction of 2 mol %.

4. A process as claimed in claims 1, 2 or 3, wherein the specific platinum-containing compound is produced by means of a powder technology synthesis process.

5. A process for producing a high-temperature superconducting, melt-textured solid material substantially as hereinbefore described in the foregoing examples.

6. A high-temperature superconducting, melt-textured solid material obtained or obtainable by a process as claimed in any one of the preceding claims.

7. A high-temperature superconducting melt-textured solid material substantially as hereinbefore described in the foregoing examples.

8. An article comprising a high-temperature superconducting, melt-textured solid material as claimed in claims 6 or 7.

9. A specific platinum-containing compound of the formula



where

SE - Y, Nd, Sm, La, Dy, Er or Gd, or a mixture of two or more of these elements and

M - Ba, Sr or Ca, or a mixture of two or more of these elements.

k - 0 to 2

l - 1 to 2

m - 2 to 4

il

$n = 1 \text{ to } 2$

and

$x = 1.5 k + m + (n + 1)z$, where $(z = 0.5...2)$,

10. Use of a specific platinum-containing compound as claimed in claim 9 for producing a high-temperature superconducting, melt-textured solid material.



The
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Application No: GB 9711677.6
Claims searched: 1 to 10

Examiner: Miss M. M. Kelman
Date of search: 26 August 1997

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C1A AVG1, C1J JES

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Other: ONLINE: CLAIMS, JAPIO, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X,E	GB 2308843 A THE TRUSTEES OF PRINCETON UNIVERSITY see page 17, lines 1 to 6	9,10
X	EP 0537363 A1 INTERNATIONAL SUPERCONDUCTIVITY TECHNOLOGY CENTER see page 3, lines 50 to 52, page 4, lines 43 to 44, and Table 1	9,10
A,P	WO 96/21252 A1 THE BOARD OF REGENTS OF THE UNIVERSITY AND COMMUNITY COLLEGE SYSTEM OF NEVADA	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.